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Oxidation behavior of Am-containing MOX fuel pellets in air

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Abstract

Americium-containing MOX (Am-MOX) fuels were subjected to heating tests using thermogravimetric and differential thermal analysis measurements in a flowing gas atmosphere of dry air to investigate the effect of Am addition on oxidation behavior of MOX fuel. Three kinds of Am-MOX fuel pellets containing 3, 5 and 10 wt.% Am were prepared for the examination together with MOX fuel and UO_2 fuel pellets as references. Sintered fuel pellets were heat-treated to adjust the oxygen-to-metal ratio to 2.00 and were crushed into small pieces. The weight gain due to oxidation was monitored and the pulverization behavior of the fuel pellets was observed. The specimens were analyzed by X-ray diffraction in order to investigate the change of the phase relation. The specimens were subjected to programmed rate heating test (6 K/min) from room temperature to 1073 K. The UO_2 pellet specimen was oxidized rapidly to an O/M ratio of 2.67 (i.e. U_3O_8 was formed) and it was pulverized easily. The specimens of MOX fuel and Am-MOX fuel pellets, however, were oxidized gradually to O/M ratio around 2.3 (i.e. MO_{2+x} and/or M_4O_9 were formed) and there was no pellet crumbling. Although the oxidation rate slightly decreased with increasing the Am content in the Am-MOX fuels, the oxidation curve shapes of Am-MOX fuels were similar to the curve of MOX fuel. The isothermal heating test was carried out for the specimens of MOX, 3 wt.% Am-MOX and 5 wt.% Am-MOX fuels. The kinetic analysis of the oxidation in the isothermal heating test was evaluated by the Johnson-Mehl equation.

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Keywords: MOX fuel; Minor Actinide; Oxidation

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1. Introduction

Uranium and plutonium mixed oxide (MOX) fuels containing several percent of minor actinides (MAs) and fission products are promising candidates for a closed nuclear cycle system based on a fast reactor [1]. Many novel and practical findings have been obtained for MA-containing MOX (MA-MOX) fuels related to items such as development of their fabrication process, measurement of several of their thermophysical and themochemical properties, and observation of their irradiation behavior [2]. In addition to the knowledge noted above, the oxidation properties of the fuels are also important for understanding the fundamental mechanism of oxidation of actinide oxides, for the design of suitable schemes for the fuel fabrication and reprocessing, and for purpose of reactor safety. Understanding of the pulverization behavior due to the change of crystal structure resulting from oxidation of the fuel is necessary to design suitable schemes for the utilization of dry recovery powders from the scrap pellet and for expediting the removal of volatile and gaseous fission products before the fuel is dissolved in nitric acid (adoptability of voloxidation). From the aspect of safety, it is desirable that the fuel pellets maintain its mechanical integrity if it is exposed to an oxidized environment at elevated temperature in the case of accident.

Although oxidation properties of UO_2 and MOX fuels in air were reported so far [3-11], no research has yet been carried out to investigate the oxidation behavior of the MA-MOX fuels. In order to accumulate the basic data and knowledge concerning the oxidation behavior of MA-MOX fuel, Am-containing MOX (Am-MOX) fuels were subjected to heating tests under the flowing gas atmosphere of dry air in the present study. The weight gain due to oxidation was monitored and the pulverization behavior of the fuel pellets was observed. The change of the phase relation of the specimens was also analyzed. The experimental results of oxidation behavior of Am-MOX fuels were compared with those of the data for UO_2 and MOX fuels.

2. Experimental

2.1. Specimens

Am-MOX fuel pellets were fabricated adopting the conventional powder metallurgy method using a remote handling technique in the shielded air-tight hot cell of the Alpha-Gamma Facility (AGF) at JAEA's Oarai Research and Development Center [12]. UO_2 powder, Am-containing UO_2 powder and two kinds of Am-containing PuO_2 powders were used as raw materials. Before the sintering step, these powders were annealed at 873 K for 2 hours in a furnace with a kanthal heater to remove absorbed moisture. After the heat pre-treatment, each powder type was weighed on an electronic balance in order to adjust the amount to the predetermined weight ratio. This was followed by mixing the desired powders in an alumina ball mill for about 5 hours without solvent (dry condition). Zinc stearate was added as a binder and the powders were further mixed for 30 minutes before cold-pressing into green pellets at a pressure of about 380 MPa. The green pellets were pre-sintered at 1073 K for 2.5 hours in the furnace with the kanthal heater to remove the binder and then were sintered at 1973 K for 3 hours in a furnace with a tungsten mesh heater. The densities of the fuel pellets were determined from dimensional and weight measurements and were found to be almost the same values of 93 ± 3 % T.D.(Theoretical Density). As references, UO_2 and MOX fuel pellets were also prepared by the same fabrication procedure. Sintered fuel pellets were heat-treated to adjust the oxygen-to-metal (O/M: M= U, Pu, Am) ratio to 2.00. The ratio was confirmed gravimetrically at room temperature. All of the heat treatments and sintering processes were carried out under a flowing gas atmosphere of Ar-5 % H_2 or Ar-0.05 % H_2. The composition of the atmosphere was controlled by adding an appropriate amount of moisture.

2.2. Heating tests

After crushing the pellets into small specimen pieces, about 50 μg of each specimen of UO_2, MOX, 3 wt.% Am-MOX, 5 wt.% Am-MOX and 10 wt.% Am-MOX fuels (Pu content : 30 wt.%) was subjected to the programmed rate heating test (6 K/min) from room temperature to 1073 K under the flowing gas atmosphere of dry air. The isothermal heating test was also carried out for the specimens of MOX, 3 wt.% Am-MOX and 5 wt.% Am-MOX fuels. Both the programmed rate and isothermal heating tests were carried out by using a thermogravimetric and

differential thermal analysis (TG-DTA) apparatus (Rigaku model TG-8120) connected with a gas supply system. Each specimen was loaded into an alumina capsule and placed in the apparatus. For reference, an alpha-alumina sample was loaded into another alumina capsule and also placed in the apparatus. In the isothermal heating test, O/M ratios were adjusted to 2.00 at each predetermined temperature at first by the adjustment of oxygen partial pressure which was done by changing the ratio of H_2O/H_2. The oxygen partial pressure was measured with a stabilized zirconia oxygen probe. After the adjustment of MO_2, the flowing gas was changed to dry air. This was the starting time of the isothermal heating test.

The specimen weight change of ±1 μg which corresponds to the O/M ratio change of ±0.0002, was able to be measured by TG analysis with a horizontal differential type balance. The O/M ratio was calculated from the weight change of the specimen using the following equation:

$$O/M = 2.00 \pm \frac{M}{16} \cdot \frac{\Delta W}{W} \tag{1}$$

where M is molecular weight of $MO_{2.00}$ (M= U, Pu, Am) , ΔW is the change of weight and W is the specimen weight of $MO_{2.00}$.

2.3. Characterization

After the heat treatment, the pulverization behavior of the fuel pellets was observed using secondary electron imaging. In addition, the un-oxidized and oxidized specimens were analyzed by X-ray diffraction (XRD) in order to investigate the change of phase relation of the specimens. A Rigaku model RAD-C system was used for the XRD measurements. Systematic peak shiftings were corrected using Si (NIST 640c) as external standard. The SEM observations were carried out using the Tiny-SEM Mighty-8 model (Technex Lab Co., Ltd.). Immediately prior to the SEM observations of the specimens, a thin film of Au–Pd was applied to their surfaces by vacuum evaporation to avoid electron charging effects.

3. Results and discussion

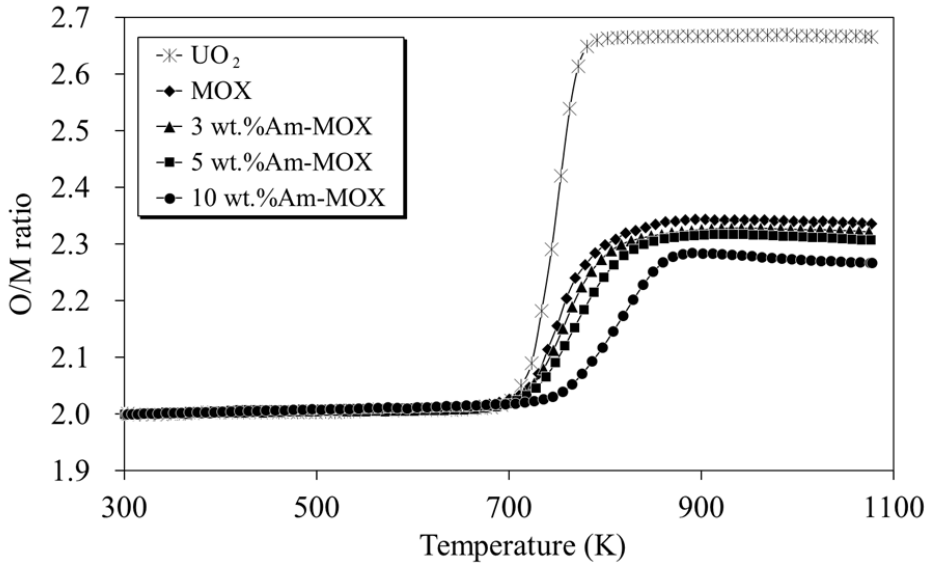
3.1. Programmed rate heating test

Fig. 1 shows the change of TG and DTA on the programmed rate heating test (6 K/ min) from room temperature to 1073 K. The weight (O/M ratio) changes of MOX fuel and Am-containing MOX fuels were smaller than that of UO_2 and the oxidation temperatures (the temperatures at which weight-gain due to oxidation started) were shifted to higher temperature. Although the increased values of weight (attained O/M ratio) and increasing rate of weight change decreased with increasing Am content in Am-MOX fuels, the oxidation curve shapes of Am-MOX fuels were similar to the MOX fuel curve shape. The values of attained O/M ratio slightly decreased with increasing temperature. It was considered that the equilibrium O/M ratio with air decreased with increasing temperature. The attained O/M ratio of UO_2 was about 2.67, while that of the other fuels was about 2.3. Benedict and Sari [3] reported that the maximum attained O/M ratio for a 30%Pu-MOX fuel specimen in air was about 2.3. The experimental results of MOX and Am-MOX fuels obtained in this study were similar to their value.

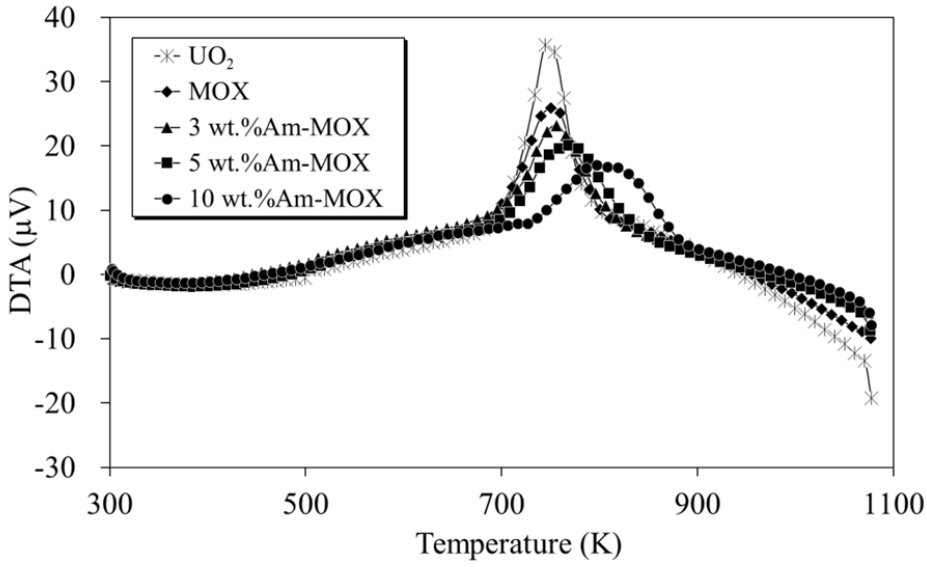
Fig.2 shows appearance of the specimens after the heat treatment. UO_2 was pulverized due to the heat treatment in the air. On the other hand, macroscopic changes were not found in the other specimens.

Fig. 3 shows the XRD patterns obtained at room temperature for each specimen. It was confirmed that the specimen which was originally UO_2 was converted to a single phase of an orthorhombic structure of U_3O_8. The XRD patterns of the other specimens after the programmed rate heating test were similar to their patterns before heating and indicated they had cubic structures, although the diffraction peaks after the test were slightly shifted in the higher angle direction. In these XRD patterns, no sign of M_3O_8 phase was found. Sari et al. [4] reported that no M_3O_8 phase was observed for the 30% Pu-MOX fuel specimen which was oxidized to the O/M ratio of 2.32. The present results of MOX and Am-MOX fuels were in accord with their findings. Table 1 shows the lattice parameters

of each specimen before and after the programmed rate heating test. The lattice parameters of the specimen which was originally UO_2 were a = 0.6715 nm, b = 1.196 nm, c = 0.4146 nm, which were in good agreement with the literature values [13]. The lattice parameters of MOX and Am-MOX fuels after this heating test decreased compared to the values before. It is reported that the excess of oxygen ion shortened the lattice parameter of MOX fuel and the contraction of lattice parameter was depended on the oxidation state of uranium [5]. Markin and Street [6] reported that the lattice parameters of MOX fuel decreased with increasing O/M ratio due to the oxidation of MO_2. The results of MOX and Am-MOX fuels obtained in this study were similar to their findings. According to the present XRD results, UO_2 was converted to U_3O_8, while the MOX and Am-MOX fuels were oxidized to MO_{2+x} or M_4O_9.



(a) TG



(b) DTA

Fig. 1. Variation of TG and DTA during the programmed rate heating test.

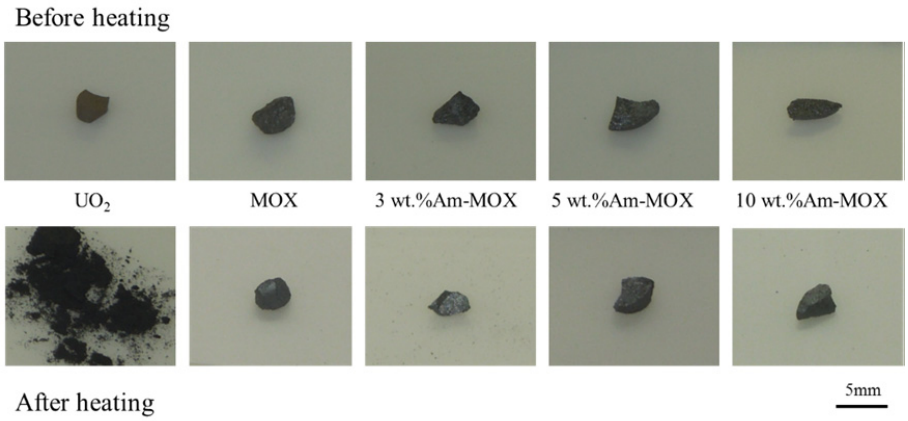


Fig. 2. Appearance of the heated specimens.

Table 1. Lattice parameters determined from XRD patterns (nm).

			UO_2	MOX	3 wt.%Am-MOX	5 wt.%Am-MOX	10 wt.%Am-MOX
Before heating			0.5471	0.5448	0.5447	0.5445	0.5441
After heating	Programmed rate		a=0.6715 b=1.1960 c=0.4146	0.5429	0.5428	0.5427	0.5426
	Isothermal	673 K	-	0.5435	0.5437	0.5437	-
		723 K	-	0.5432	0.5432	0.5431	-
		773 K	-	0.5431	0.5431	0.5430	-
		873 K	-	0.5433	0.5434	0.5433	-

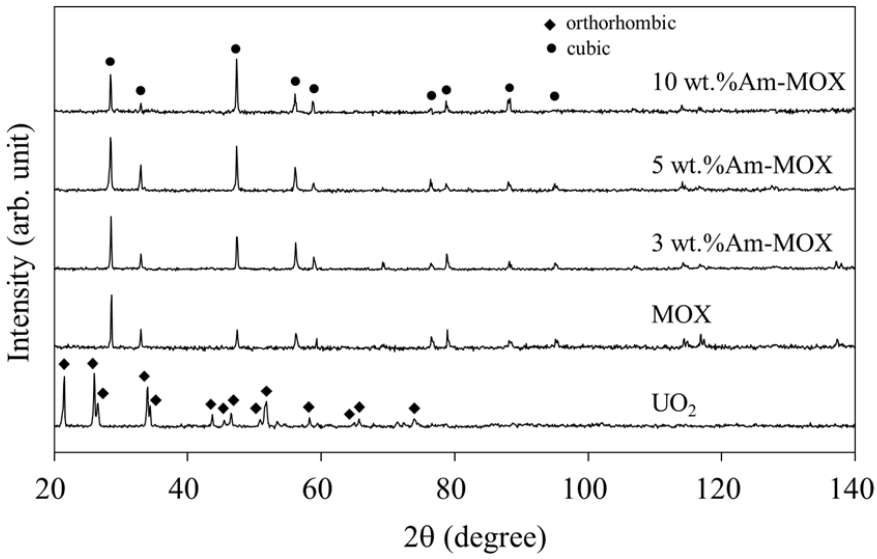


Fig. 3. XRD patterns obtained at room temperature for each specimen.

Fig. 4 shows the SEM images on the specimens before and after the programmed rate heating test. The spallation particles of heat-treated UO_2 specimen had highly fractured micro cracked features (Fig.4 (a)). The non-pulverized specimens, the MOX and Am-MOX fuels, were mechanically crushed after this heating test and their fracture surfaces were observed by SEM. As shown in Figs. 4 (b)-(e), apparent grain boundary facets were observed and there was no sign of intragranular volume expansion. It is worth noting that the oxidized specimens of MOX and Am-MOX fuels did not transform to powder, as would be expected from a complete transformation to the less dense phase M_3O_8.

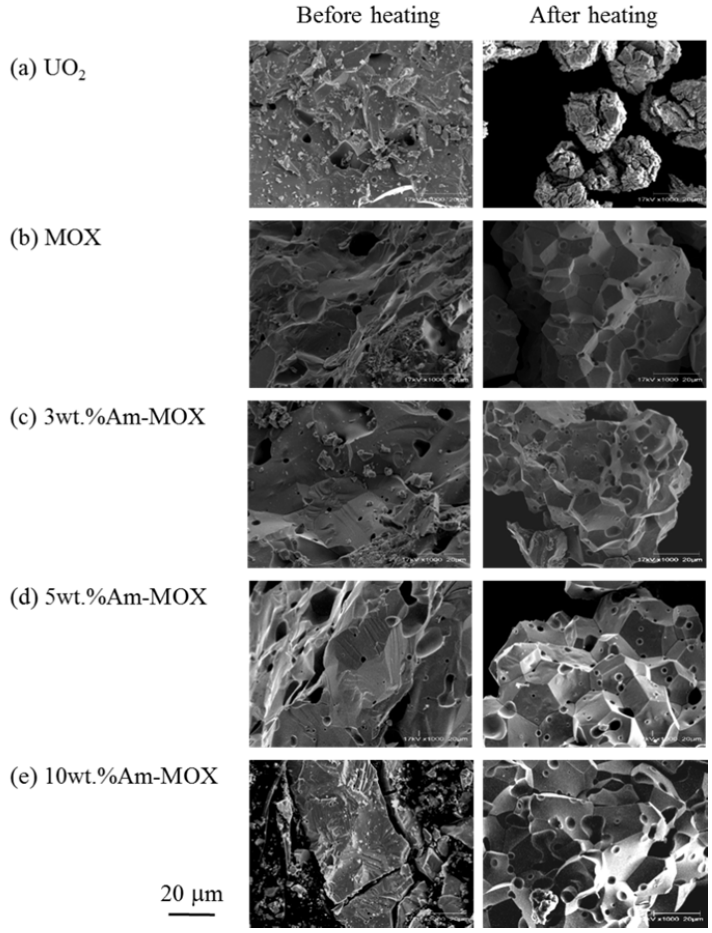
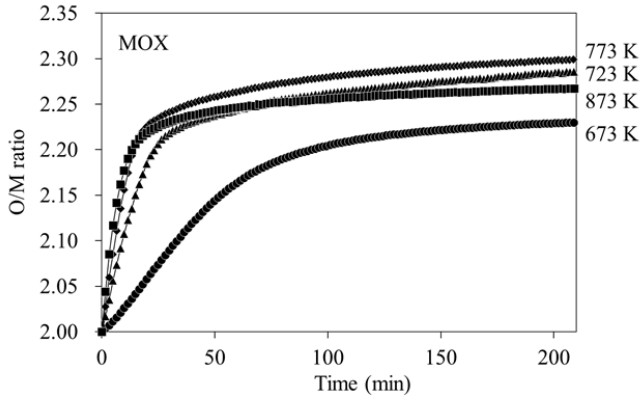


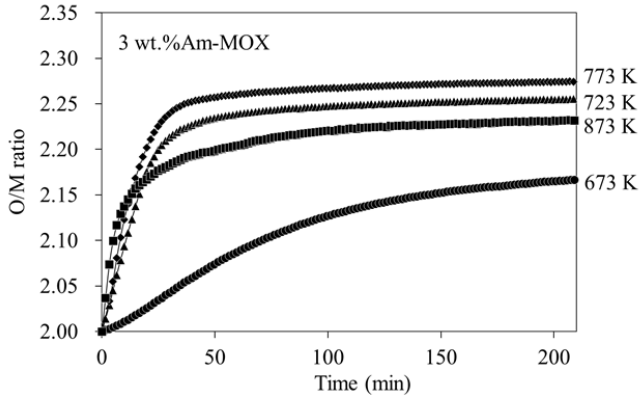
Fig. 4. SEM images on the specimens before and after the programmed rate heating test.

3.2. Isothermal heating test

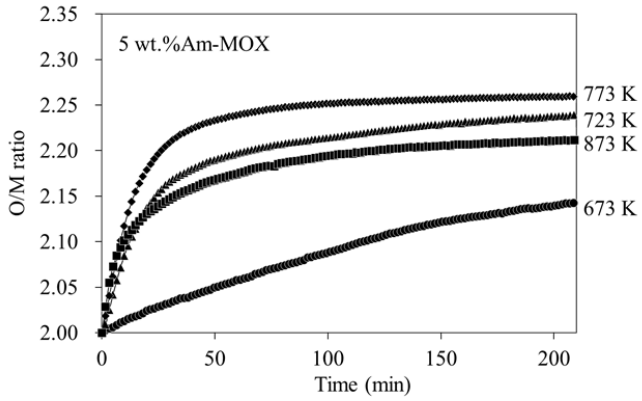
Fig. 5 shows the TG variations during the isothermal heating test for MOX, 3 wt.% Am-MOX and 5 wt.% Am-MOX fuels. The origin of the horizontal axis is the starting time of the dry air flow. The weight of each specimen gradually increased with time at 673 K. At temperatures higher than 673 K, the increase rates of the weight of each specimen abruptly increased at the beginning of the isothermal heating test. Although the attained O/M ratio slightly decreased with increasing Am content in the Am-MOX fuel specimens, the weight variation behavior due to oxidation of the Am-MOX fuels was similar to that of MOX fuel. Fig. 5 also indicates that the increase rate of O/M ratio of MOX and Am-MOX fuels at 873 K is higher at the beginning of the isothermal heating test, then the graph curves become gentle.



(a) MOX



(b) 3 wt.% Am-MOX

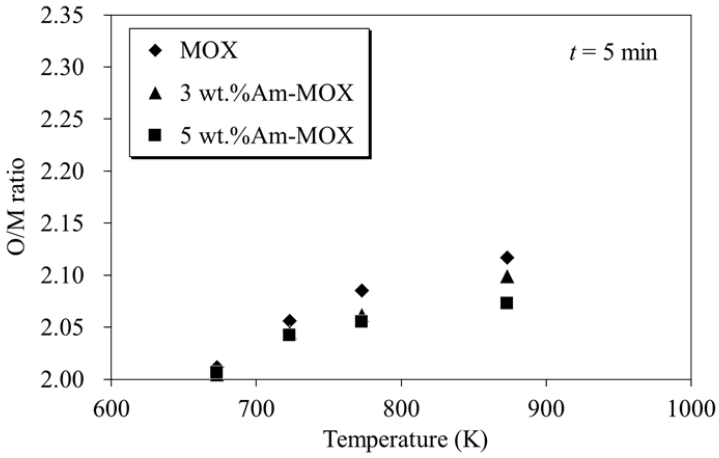


(c) 5 wt.% Am-MOX

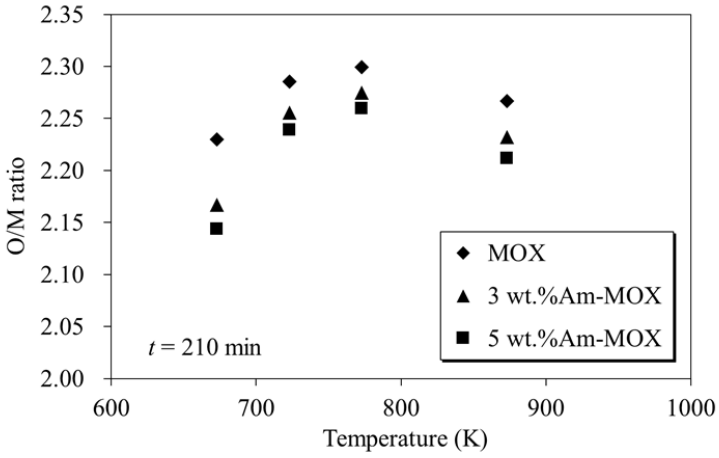
Fig. 5. TG variations during the isothermal heating test for MOX, 3 wt.% Am-MOX and 5 wt.% Am-MOX fuels.

The lattice parameters of the specimens after the isothermal heating test are also listed in Table 1. The lattice parameters decreased compared with the values before. The result is similar to that of the programmed heating test. In these specimens, the observed diffraction peaks were only due to the cubic structure. The attained O/M ratio and XRD patterns implied that MOX and Am-MOX fuels, which originally have the chemical formula of MO_2, were oxidized to MO_{2+x} or M_4O_9 after the isothermal heating test. These results were similar to the phase relations which were estimated by the phase diagram of 30%Pu-MOX fuel in the literature [3-8].

Fig. 6 (a) shows the relationship between temperature and O/M ratio at 5 min after the isothermal heating test start. The O/M ratio gradually increased with increasing temperature. Fig. 6 (b) shows the attained O/M ratio at 210 min after the test start. For each specimen, the O/M ratio increased with increasing temperature to around 773 K, then decreased. This tendency has been found in the isothermal heating test of $(U_{0.75}Pu_{0.25})$ O_2 fuels in the literature [9, 10]. In this study, small piece of cracked pellets were subjected to the heating test. The highly oxidized layer, therefore, would be formed in the surface of the specimen in the case of higher temperature at 873 K and the layer delayed the oxidation of the fuels resulting in the lowering the attained O/M ratio.



(a) At 5 min



(b) At 210 min

Fig. 6. Relationship between temperature and attained O/M ratio.

3.3. Oxidation rate

The Johnson-Mehl equation [14] has been used for the evaluation of the oxidation rate of UO_2 fuel [11]. In order to analyze the oxidation data of MOX and Am-MOX fuels, the equation was applied in this study. The Johnson-Mehl equation is given by:

$$\log\frac{1}{1-y} = \frac{1}{2.303}\cdot k^n \cdot t^n \tag{2}$$

where y is the degree of reaction, t is the reaction time, k is the rate constant and n is the exponent of t. In this equation, k and n are assumed to be independent of y. Equation (3) is obtained by taking the logarithms of both sides of equation (2).

$$\log\log\frac{1}{1-y} = n\log t + n\log k - \log 2.303 \tag{3}$$

If a reaction can be described by the Johnson-Mehl equation, a graph of log log [1/(1-y)] vs. log t will be linear. Fig. 7 shows a plot of log log [1/(1-y)] vs. log t for the 3 wt.% Am-MOX fuel as an example. The linearity was good at the initial stage of the reaction. A similar tendency was found in the data of the other fuels. This implied that the data on oxidation reactions of MOX and Am-MOX fuels obtained in this study were described by the rule expressed by Johnson-Mehl equation. The values of n and k, which were estimated from the slope and the intercept with the ordinate obtained extrapolation, are indicated in Table 2. The values of n ranged between 1.0 and 1.2. It was reported that the time exponent n in the Johnson-Mehl equation is closely correlated with the difference in type of reaction model, the value of n is 1.5 for diffusion-controlled growth and 3.0 for the growth controlled by the interface process [14]. The values of n obtained in this study were similar to the values which represent the diffusion controlled process. The values of k increased with increasing temperature indicating the reaction rate was higher at higher temperatures.

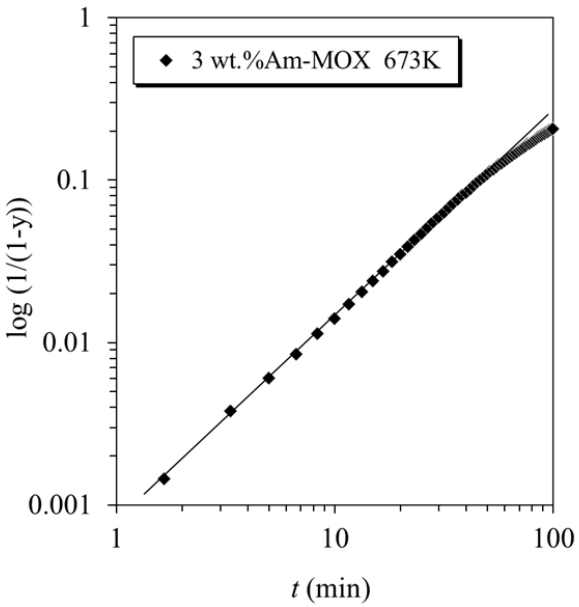


Fig. 7. Example of the analysis by the Johnson-Mehl equation for the 3 wt.% Am-MOX fuel.

Table 2. Summary of the exponent of time, reaction rate and activation energy values.

	Temperature T (K)	Exponent of time n (-)	Reaction rate k (min^{-1})	Activation energy Q (kcal/mol)
MOX	673	1.20	1.52E-02	19.6
	723	1.10	3.68E-02	
	773	1.10	8.35E-02	
	873	1.02	1.27E-01	
3 wt.% Am-MOX	673	1.18	8.72E-03	21.9
	723	1.05	2.33E-02	
	773	1.13	5.36E-02	
	873	1.09	1.02E-01	
5 wt.% Am-MOX	673	1.03	5.03E-03	22.9
	723	1.09	1.70E-02	
	773	1.13	3.62E-02	
	873	1.01	9.05E-02	

In general, the reaction rate k_i at temperature T_i is expressed by following Arrhenius equation:

$$k_i = A\exp\left(-\frac{Q}{RT_i}\right) \tag{4}$$

where, Q is the activation energy, R is the gas constant, and A is a constant.

Equation (5) is a variation of equation (4).

$$\ln k_i = -\frac{Q}{RT_i} + \ln A \tag{5}$$

Activation energy, shown by the slope of the Arrhenius plot (the values of k as a function of reciprocal temperatures), was obtained. Table 2 also summarizes the activation energies of the reaction. Although the activation energy slightly increased in the order of MOX, 3 wt.% Am-MOX and 5 wt.% Am-MOX fuels, each value was close to the literature data of activation energy for oxygen diffusion in hyper-stoichiometric MOX fuels [15]. These findings, such as the values of the time exponent n and the activation energy of the reaction Q, showed that the increment of the weight of MOX, 3 wt.% and 5 wt.% Am-MOX fuels during the isothermal heating test under dry air was controlled by oxygen diffusion.

4. Conclusion

Am-MOX fuels were subjected to heating tests using TG-DTA under the flowing gas atmosphere of dry air. The weight gain due to oxidation was monitored and the pulverization behavior of the fuel pellets was observed using SEM and the un-oxidized and oxidized specimens were analyzed by X-ray diffraction in order to investigate the change of their phase relation. Three kinds of Am-MOX fuel pellets containing 3, 5 and 10 wt.% Am were prepared together with the MOX fuel and UO_2 fuel pellets as references. Sintered fuel pellets were heat-treated to adjust the O/M ratio to 2.00 and then they were crushed into small specimen pieces. The specimens were subjected to the programmed rate heating test from room temperature to 1073 K. The UO_2 specimen oxidized rapidly to an O/M

ratio of 2.67 (i.e. U_3O_8 was formed) and pulverized. The specimens of MOX and Am-MOX fuels, however, oxidized gradually to the O/M ratio around 2.3 (i.e. MO_{2+x} and/or M_4O_9 were formed) without crumbling. Although the oxidation rate slightly decreased with increasing Am content in the Am-MOX fuels, the oxidation curve shapes of Am-MOX fuels were similar to the curve shape of MOX fuel. The isothermal heating test was carried out for the specimens of MOX, 3 wt.% Am-MOX and 5 wt.% Am-MOX fuels. The kinetic analysis of the oxidation in the isothermal heating test was done using the Johnson-Mehl equation. The reaction rate at the initial stage of oxidation was found to be well expressed by the equation. The activation energies of the oxidation of MOX, 3 wt.% Am-MOX and 5 wt.% Am-MOX fuels were determined and found to be almost the same magnitude as the activation energies of oxygen bulk diffusion in hyper-stoichiometric MOX fuels which were reported in the literature. From these results, it could be said that the oxidation behavior of MOX fuels was not affected so much by the addition of Am and the MOX and Am-MOX fuels containing 30 wt.% Pu and up to 10 wt.% Am did not disintegrate its shape after the oxidation test.

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